I. RESTRICTION OF ROTATION OF BIPHENYLS BY MEANS OF A MANY-MEMBERED RING THROUGH THE 3,3′-POSITIONS

II. ADDENDUM

BY

NATHAN KORNBLUM

B.S., New York University, 1935

M.S., New York University, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS,

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I. RESTRICTION OF ROTATION OF BIPHENYLS BY MEANS OF MANY-MEMBERED RING THROUGH 3,3′-POSITIONS.

INTRODUCTION

Restricted rotation has been produced in a larger number of biphenyls by means of suitable substituents in the *ortho* positions. The present work has been concerned with the possibility of producing restricted rotation in biphenic acid by means of many-membered bridge across the 5,5′-positions of this molecule. Resolution of such compounds would be a demonstration of a rather novel type of steric hindrance.

EXPERIMENTAL AND DISCUSSION

In order to establish the fact that a decamethylenedioxy chain could bridge the 3,3′-positions of biphenyl the following sequence was carried through: *o*-dianisidine⟶ 3,3′-dimethoxybiphenyl⟶ 3,3′-dihydroxybiphenyl⟶ 3-hydroxy-3′-(ω-bromo-*n*-decyloxy)-biphenyl⟶ 3,3′-(decamethylenedioxy)-biphenyl. The last step required the use of the high-dilution technique[1] in order to prevent polymerization.

The next goal was the synthesis and resolution of 2,2′-dicarboxy-5,5′(decamethylenedioxy)-biphenyl. This was accomplished as follows: *p*-cresol⟶ 3-nitro-4-hydroxytoluene⟶ 2,2′-dimethyl-4,4′-diamino-5,5′-dimethoxybiphenyl⟶ 2,2′-dimethyl-5,5′-dimethoxybiphenyl⟶ 2,2′-dimethyl-5,5′-dihydroxybiphenyl⟶ 2,2′-dimethyl-5-hydroxy-5′-(ω-bromo-*n*-decyloxy)-biphenyl⟶ 2,2′-dimethyl-5,5′-(decamethylenedioxy)-biphenyl⟶ 2,2′-dicarboxy-5,5′-(decamethylenedioxy)-biphenyl. Resolution was affected by means of the dibrucine salt. The free acid has a specific rotation of +93.3°. After seventy-two hours at room temperature the rotation fell to zero.

The resolution of 2,2′ dicarboxy-5,5′-(octamethylenedioxy) biphenyl was attempted via the brucine salt. No evidence of separation into diastereoisomeric forms was obtained and there was no evidence of mutarotation in any of the salt fractions. Decomposition of the salt gave the inactive acid. This failure to resolve the octamethylenedioxy acid should not be taken to mean that its

resolution is impossible. Other alkaloid salts must be prepared and subjected to fractional crystallization in order to establish this point.

The resolution of 2,2′-dicarboxy-5,5′-(decamethylenedioxy)-biphenyl demonstrates that a many-membered ring is capable of restricting the rotation of the benzene nuclei of the biphenyl system.

II. ADDENDUM
THE USE OF HYPOPHOSPHOROUS ACID IN DEAMINATING BENZIDINE DERIVATIVES

INTRODUCTION AND HISTORICAL

In the work of Part I it was necessary to deaminate benzidine derivatives. The usual, and not very satisfactory procedure has has been to tetrazotize and heat with ethanol.[2]

Mai[3] reported that when benzidine was tetrazotized and then treated with hypophosphorous acid, a 60 per cent yield of biphenyl was obtained. In the present work, substituted benzidines were deaminated, in good yields, by this procedure.

EXPERIMENTAL AND DISCUSSION

The tetrazonium salts obtained from *o*-dianisidine, *o*-tolidine and 2,2′-dimethyl-4,4′-diamino-5,5′-dimethoxybiphenyl were readily reduced by 30 per cent aqueous hypophosphorous acid solution to the corresponding hydrocarbons. Yields of 68-83 per cent of purified products were obtained. Not only are the yields higher than those obtained with ethanol, but the procedure is simpler, and the products are of better quality.

BIBLIOGRAPHY

[1] Luttringhaus and Ziegler, Ann., 528, 155 (1937).

[2] Saunders, "The Aromatic Diazo Compounds," p. 144-146, Longmans Green and Co., London, 1936.

[3] Mai, Ber. 35, 162 (1902).

VITA

The writer was born in New York City on March 22, 1914. He received his elementary education in the public schools of New York and graduated in 1930 from DeWitt Clinton High School in that city. He received the degree of Bachelor of Science in Chemistry in 1935 and the degree of Master of Science in 1937 from New York University. From 1935 to 1937 he was a graduate assistant in Chemistry at New York University. His graduate work was continued at the University of Illinois, where he held the appointment of Assistant in Chemistry for the years 1938-1940.